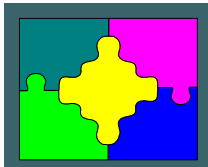


Multivariant Measurement
Methods Group

NIST
National Institute of
Standards and Technology

Investigating Crystallization in Thin Films using High Throughput Methodologies

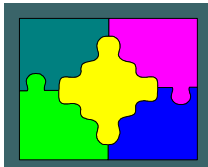
Isotactic Polystyrene

Kathryn L. Beers, Jack F. Douglas, Eric J. Amis and Alamgir Karim

National Institute of Standards and Technology
Polymers Division

NIST Combinatorial Methods Center Kick-Off Meeting
January 2002

Semi-crystalline Polymer Thin Films



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Industrial Motivation:

- Semicrystalline commodity materials (PP/PE, PLA, PC, PEG, …)
- Effect control of mechanical and optical properties, conductivity and permeability

Scientific Issues:

- Cooperativity in chain folding and diffusion, lamellar thickening, fractionation
- Molecular self-assembly
- Control of pattern formation $\rightarrow$ molecular architecture

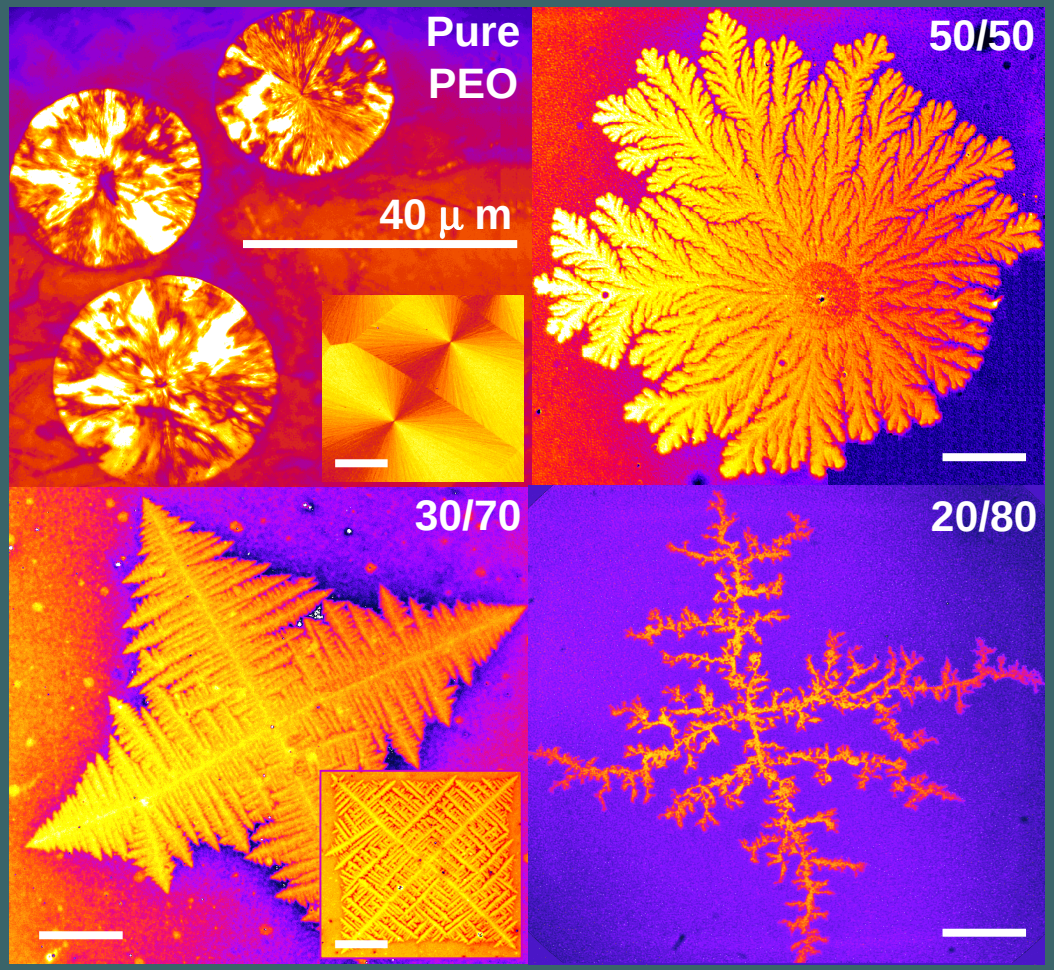
Objectives:

- Establish relevant length scales in model thin films for dominant forces influencing crystallization rate and morphology

Amorphous / Semi-crystalline Polymer Blends

PMMA/PEO Blends in Thin Films:

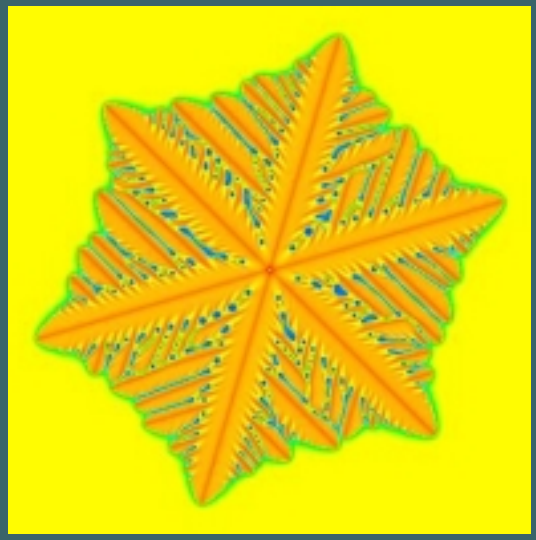
- Crystallization patterns tuned through polymer composition
- Competition with phase separation (below UCST) changes ε
- High F_{PMMA} leads to fractal dendrites (diffusion limited aggregation)



Ferreiro et al.,*Phys. Rev. E*, submitted.

Modeling Morphologies

- Model simulations based on solidification in two-dimensional fluid mixtures (Cu-Ni alloys)
- Varying ε, seaweed and dendrite structures are obtained
- No spherulitic (elasticity) or fractal morphologies to date

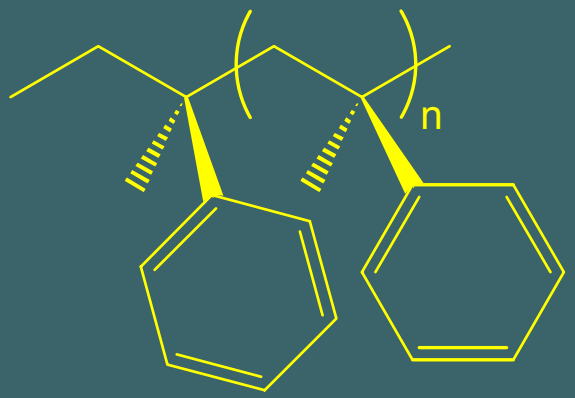


Phase-Field Simulated Hexagonal Dendrite (J. Warren)

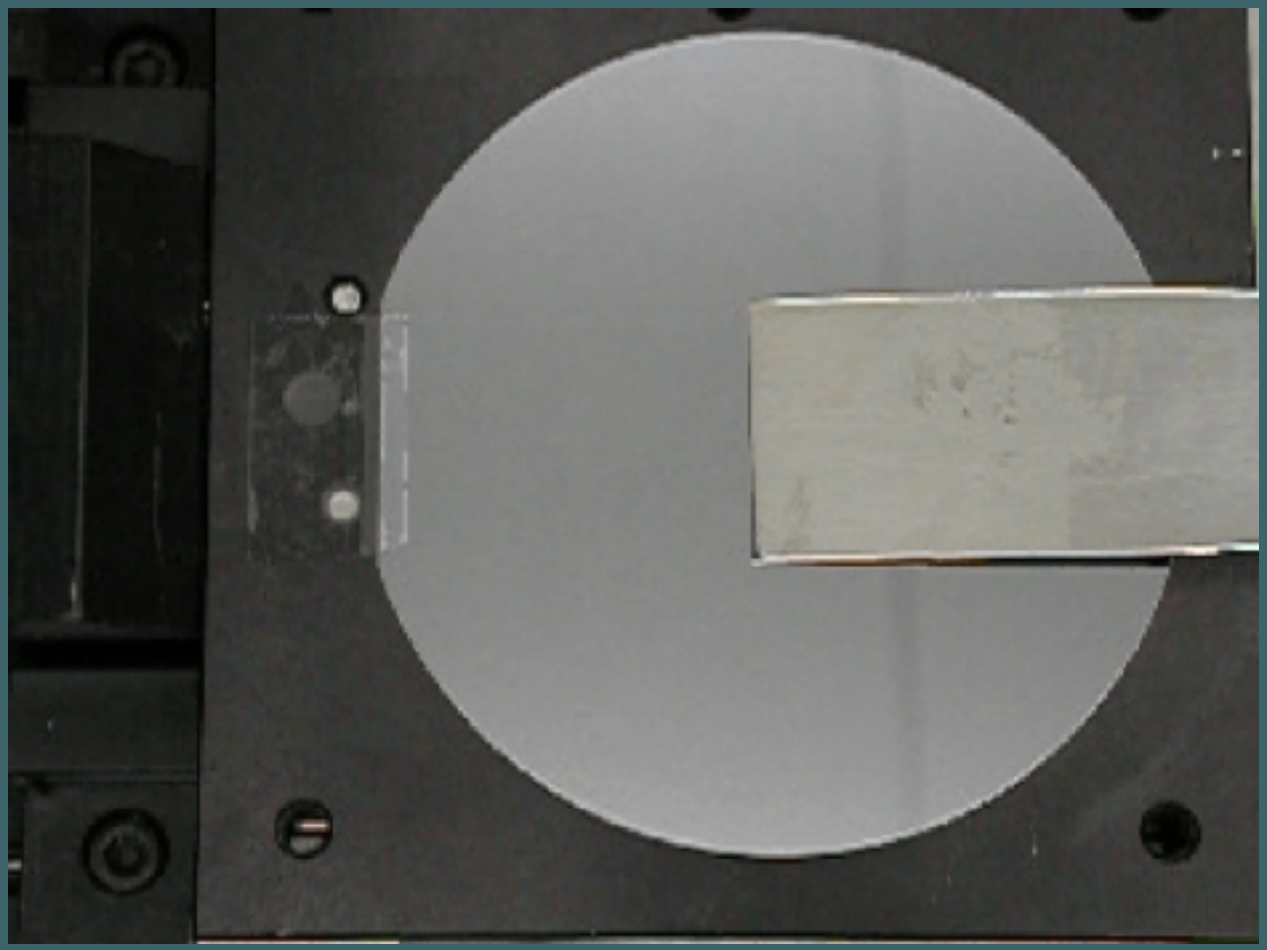
J. A. Warren and W. J. Boettinger, *Acta Metall. Mater.*, **1995**, *43*, 689.

Why Isotactic Polystyrene (ipS)?

- Substantial literature on the crystallization of ipS in bulk and thin films
- ipS crystallizes slowly and on timescales measurable by "high-throughput" optical microscopy
- high T_g: Films quenched at room temperature
- Temperature stage spans T_g to near T_m (218 °C)

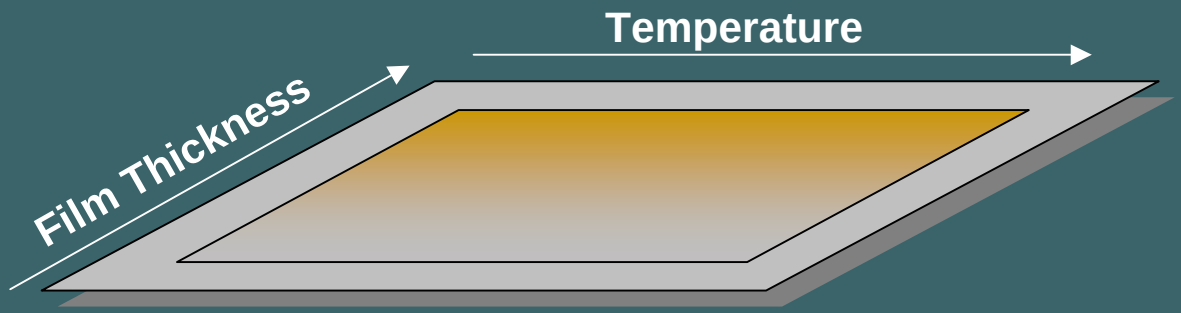


Flow Coating

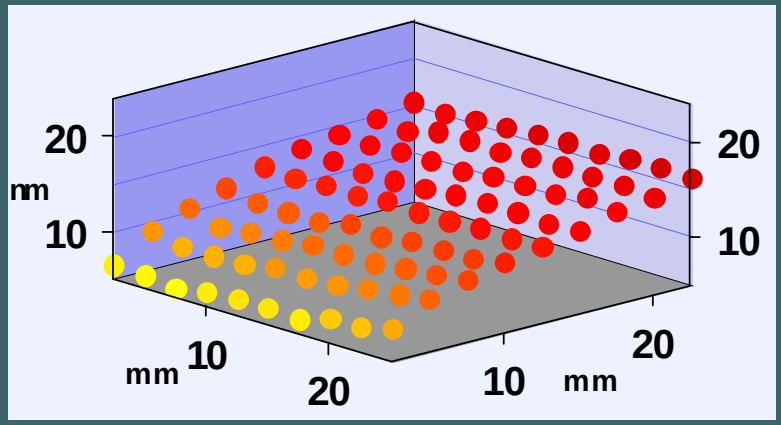


Combinatorial / High-throughput Polymer Crystallization

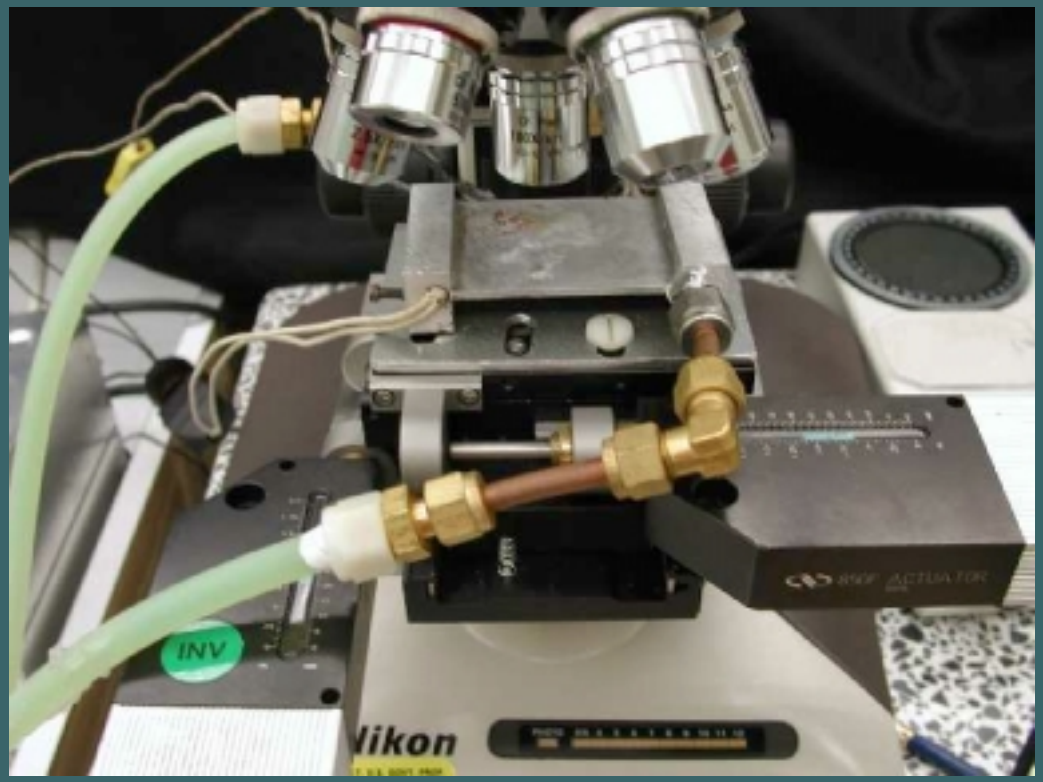
- Access to larger parameter space
- Faster
- Cheaper

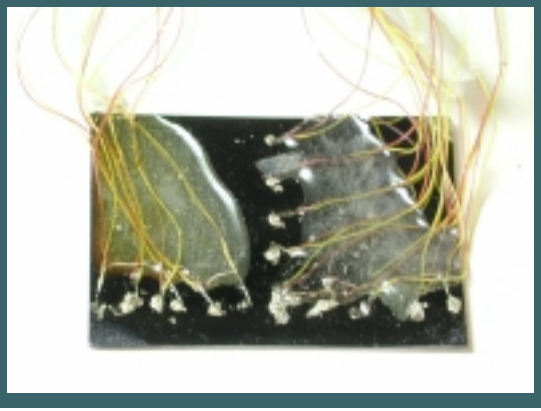


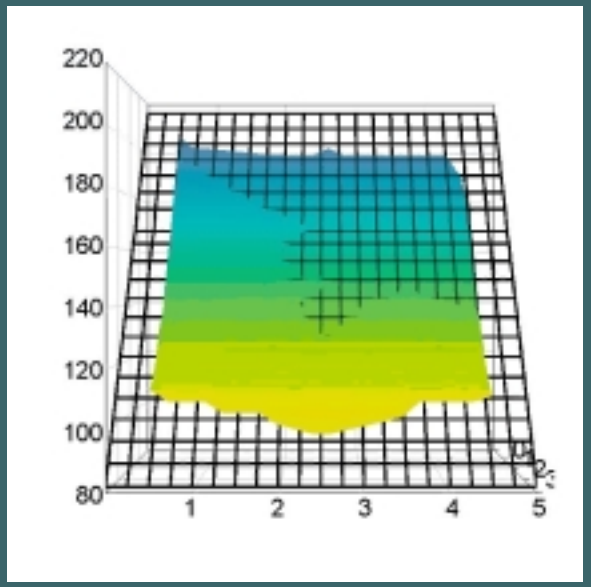
- Potential to Investigate multiple parameters:
  - Under-cooling temperature
  - Film thickness
  - *Nucleating agents*
  - Surface energy gradients
  - Surface pattern gradients



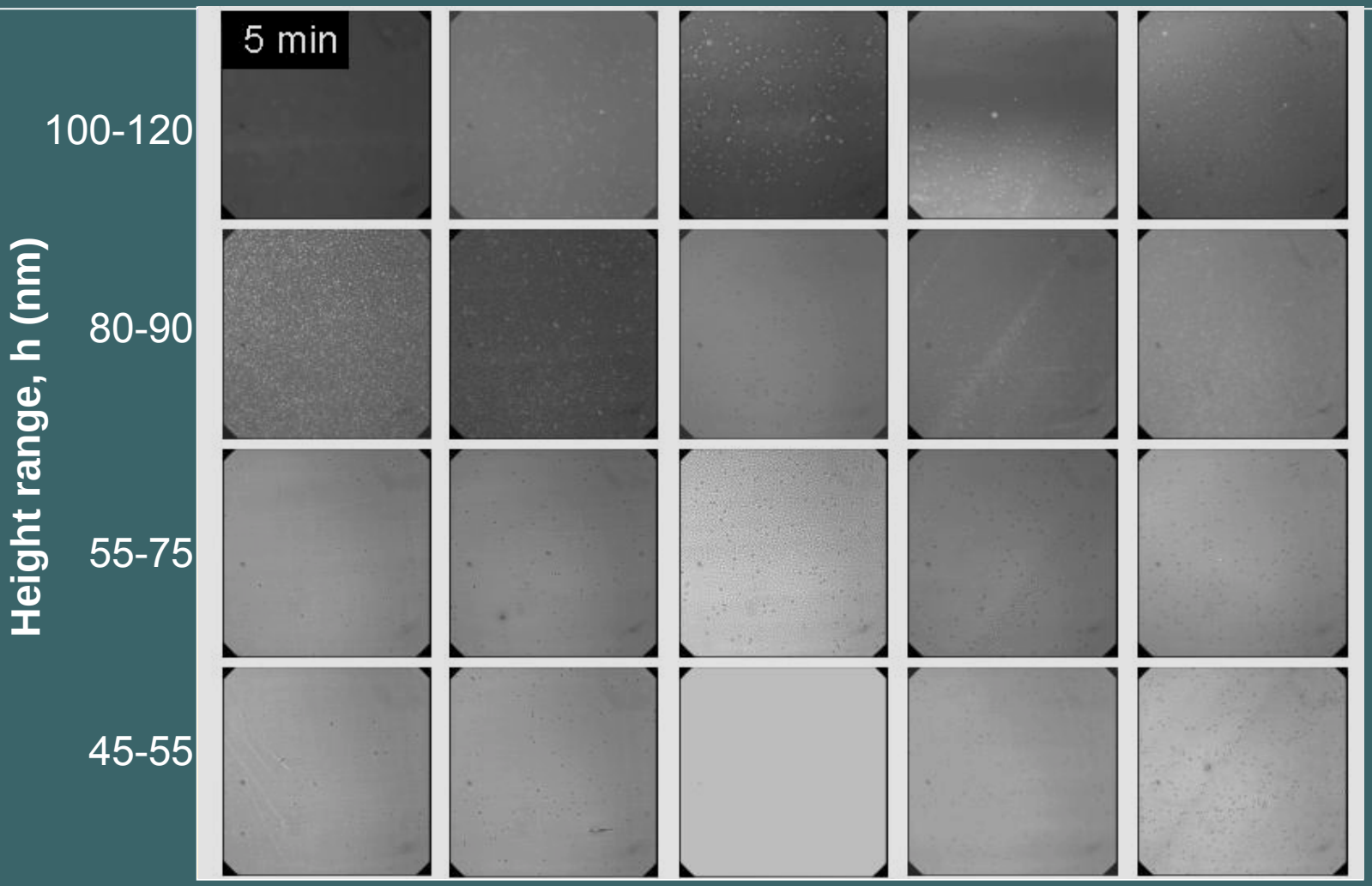
Temperature Gradient Stage





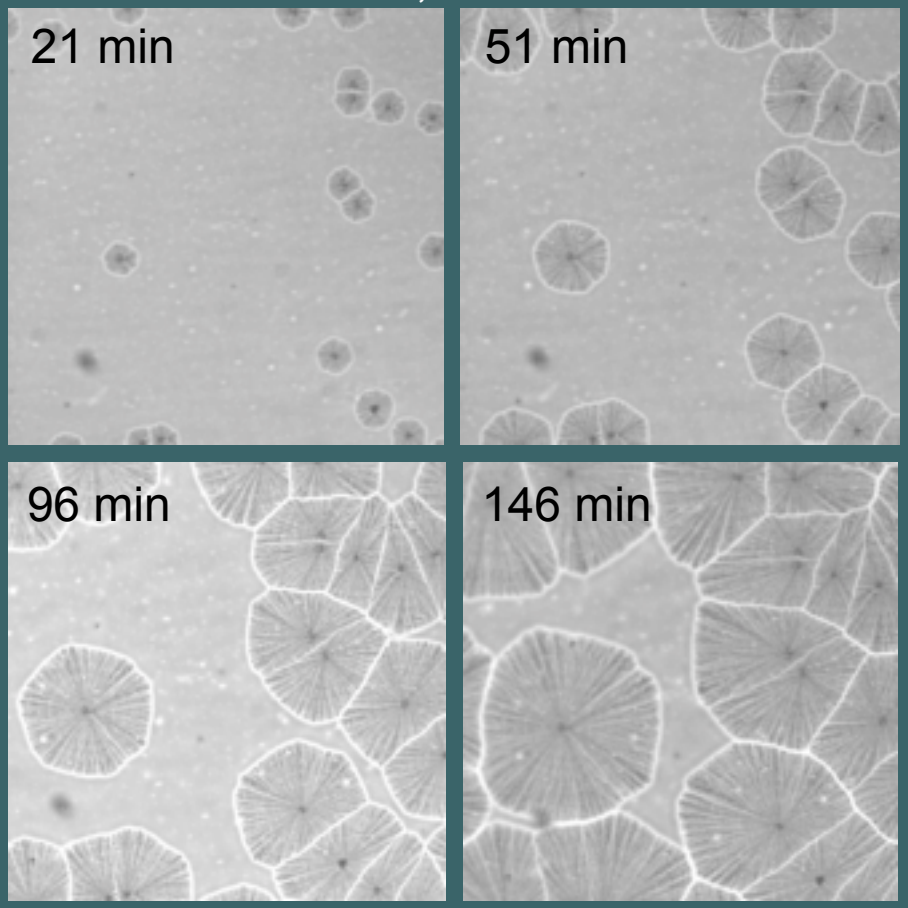


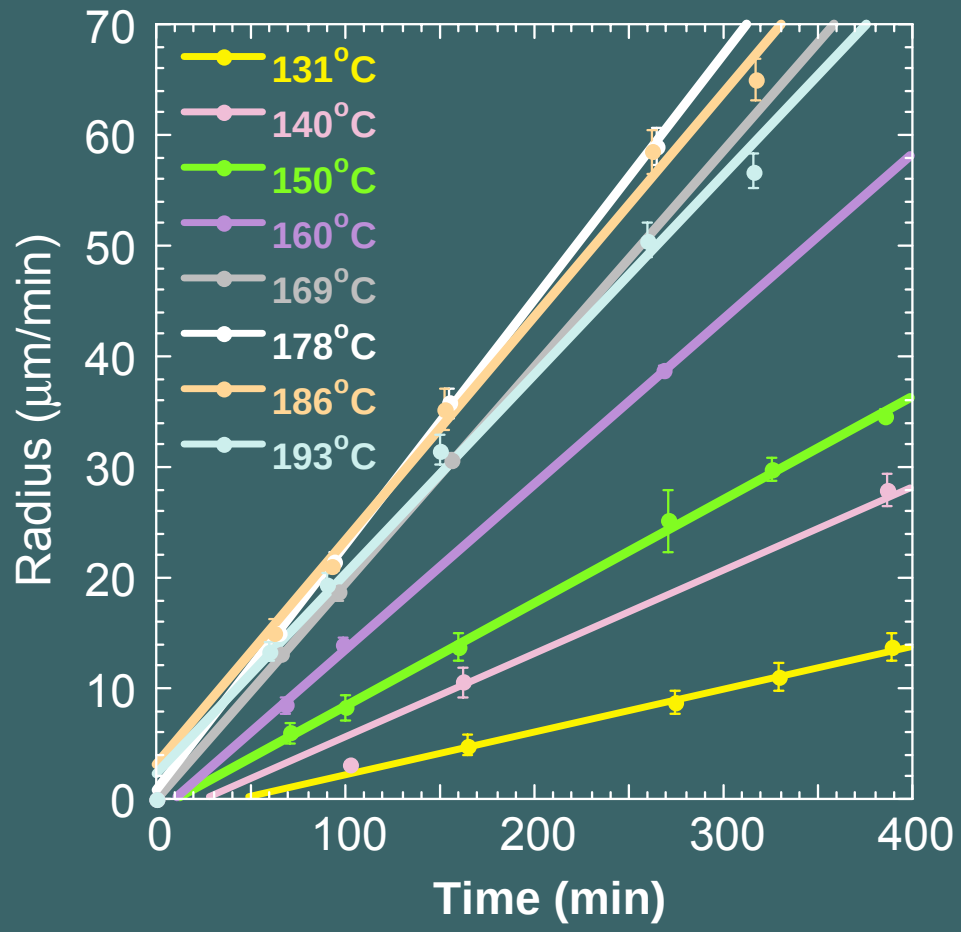
Optical Image Library



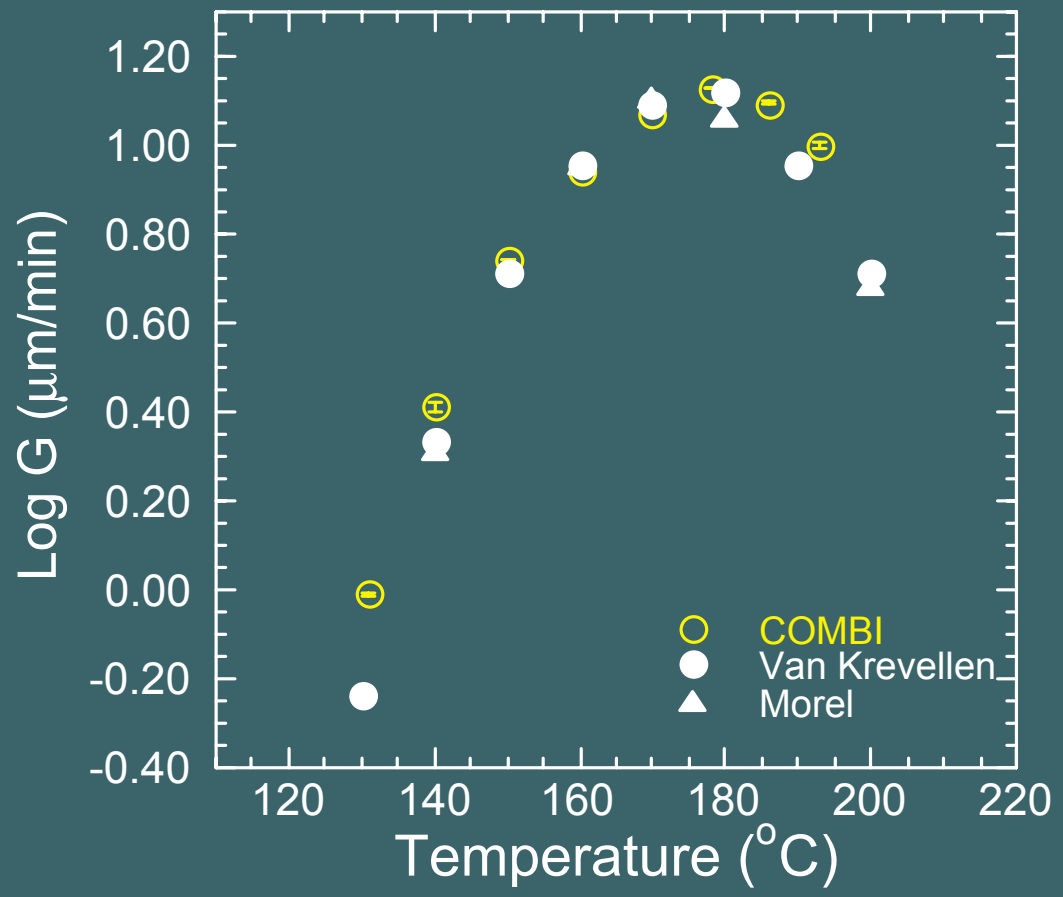
Effects of T on Growth Rates, G

T = 170°C; h = 45 nm



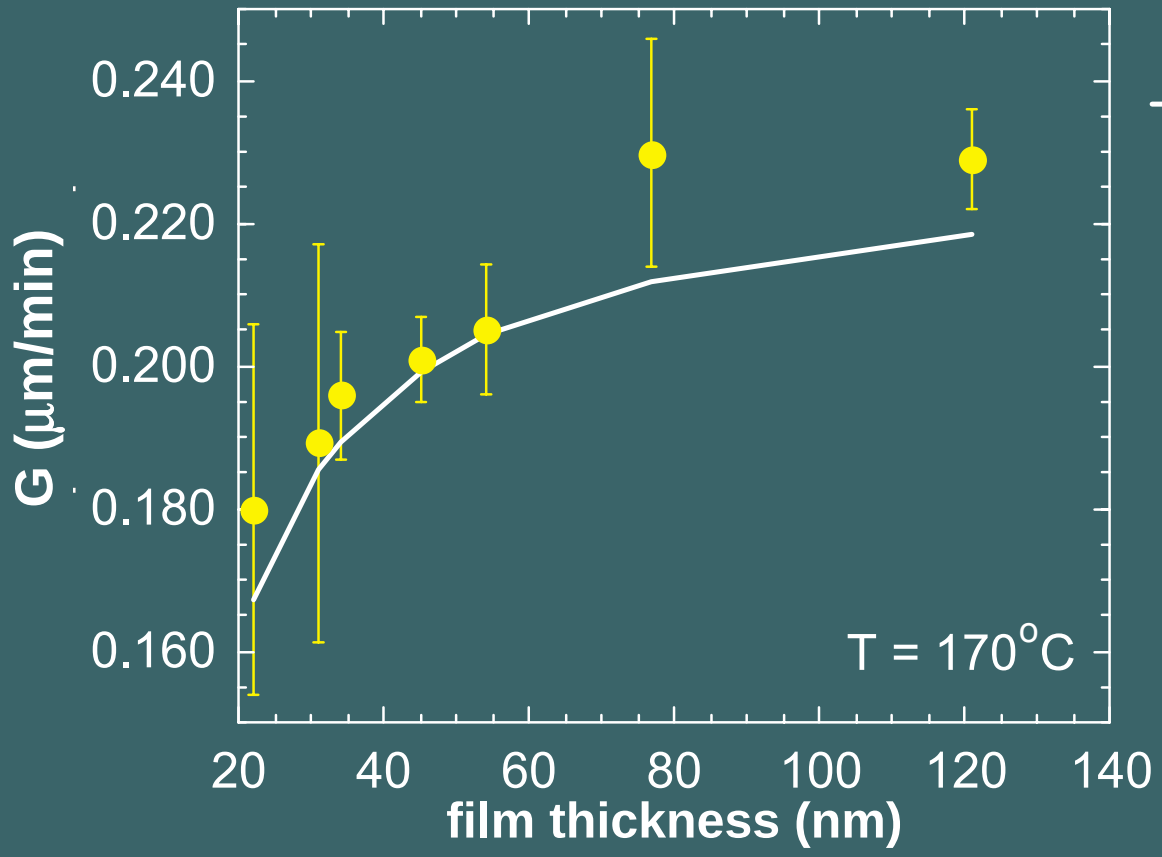


Effects of T on Growth Rates



J. Boon, *et al*., *J. Poly. Sci. A-2*, **1968**, *6*, 1791.

Effects of h on Growth Rates



Dependence of rate on film thickness:

$G(h) = G(\infty)(1-d/h)$*

*S. Sawamura, *et al*., *J. Phys. Soc. Jpn*., **1998**, *67*, 3338.

Effects of T on Structure (h > 23 nm)

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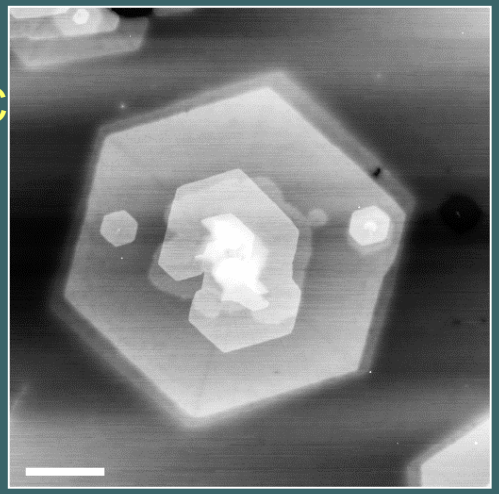
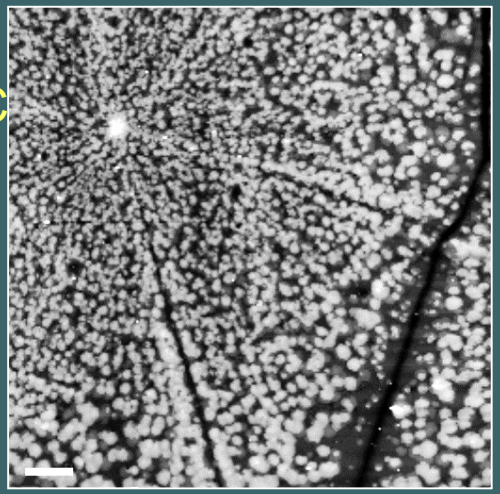
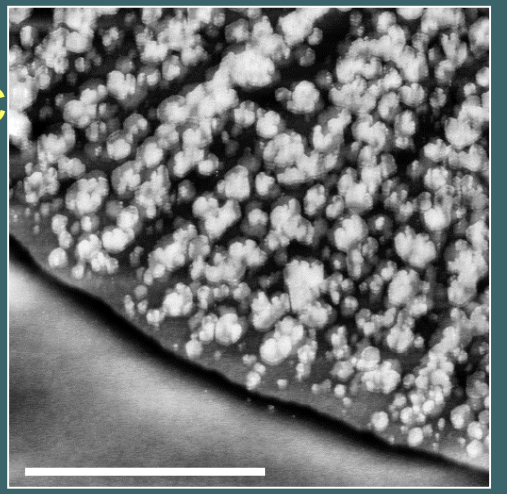
T = 202°C



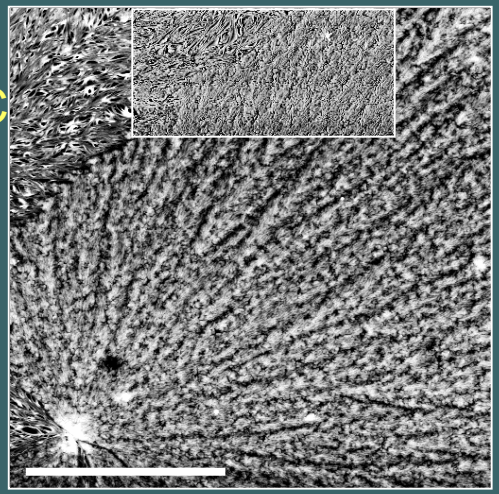
T = 193°C



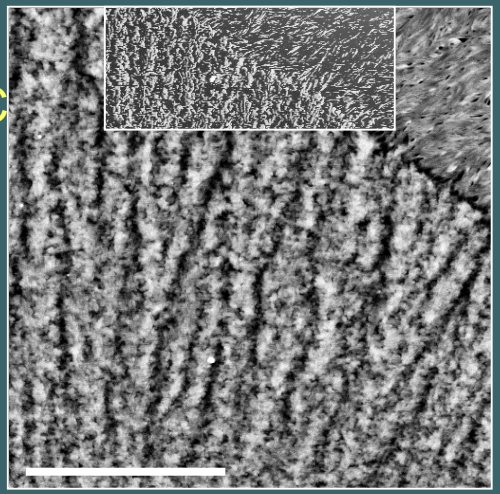
T = 169°C



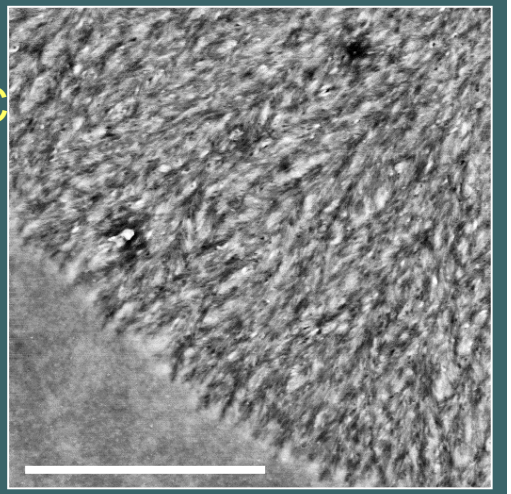
T = 160°C



T = 150°C



T = 131°C



Scale Bars: 5 μm

Effects of h on Structure

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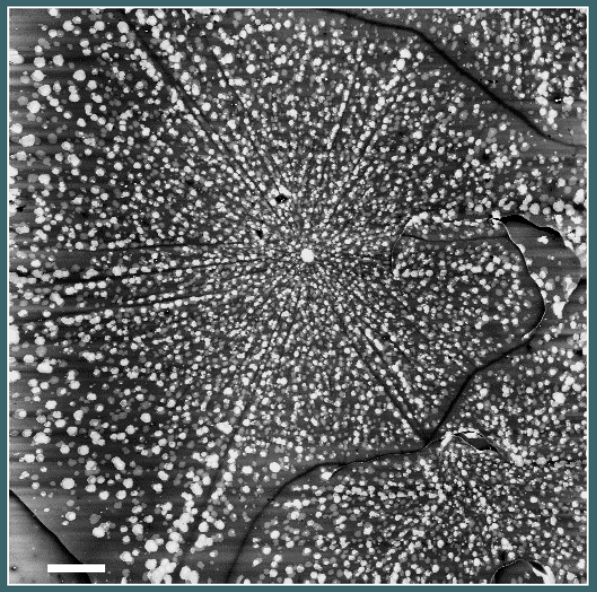
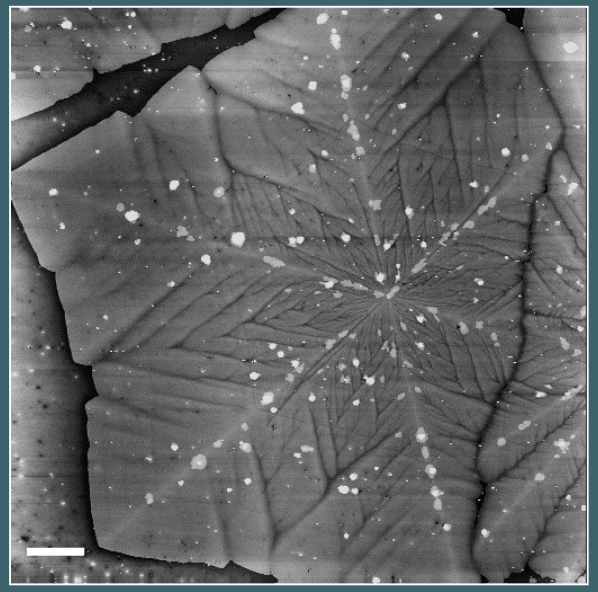
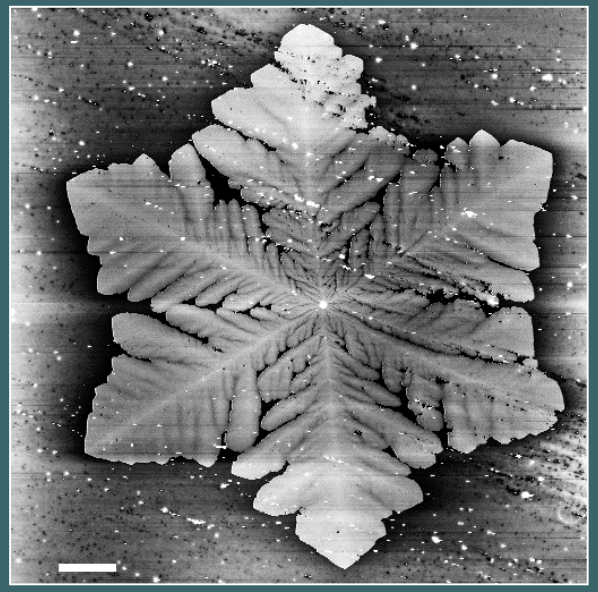
T = 186°C
h = 24 nm



T = 186°C
h = 19 nm



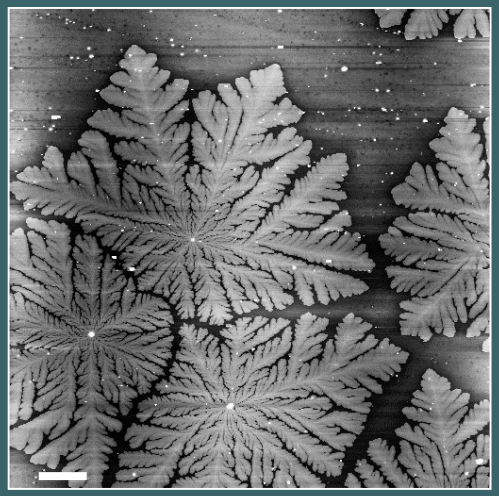
T = 186°C
h = 15 nm

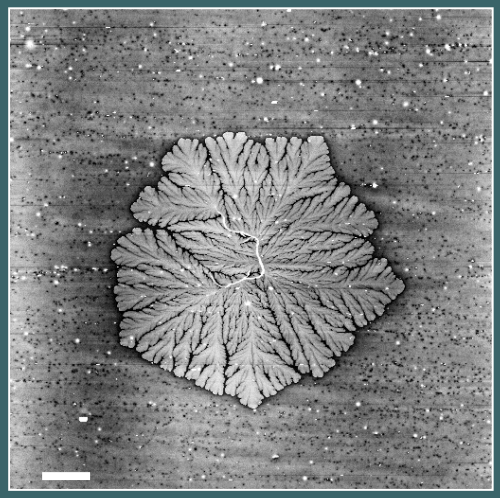


Scale Bars: 10 μm

Effects of T on Dendritic Structures

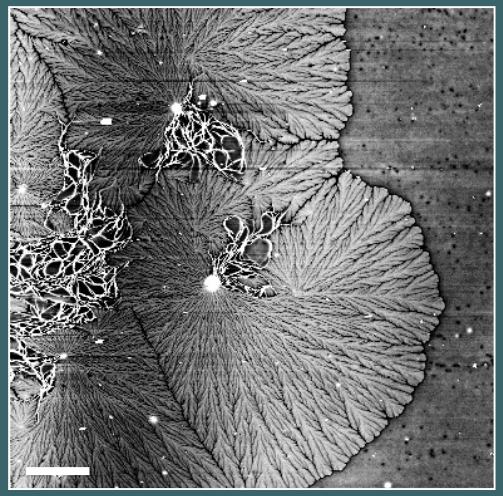
T = 169°C

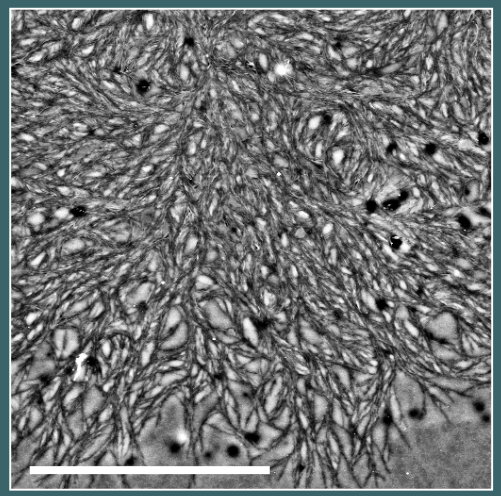




T = 160°C

T = 150°C





T = 131°C

Scale Bars: 10 μm

Structural Control Factors

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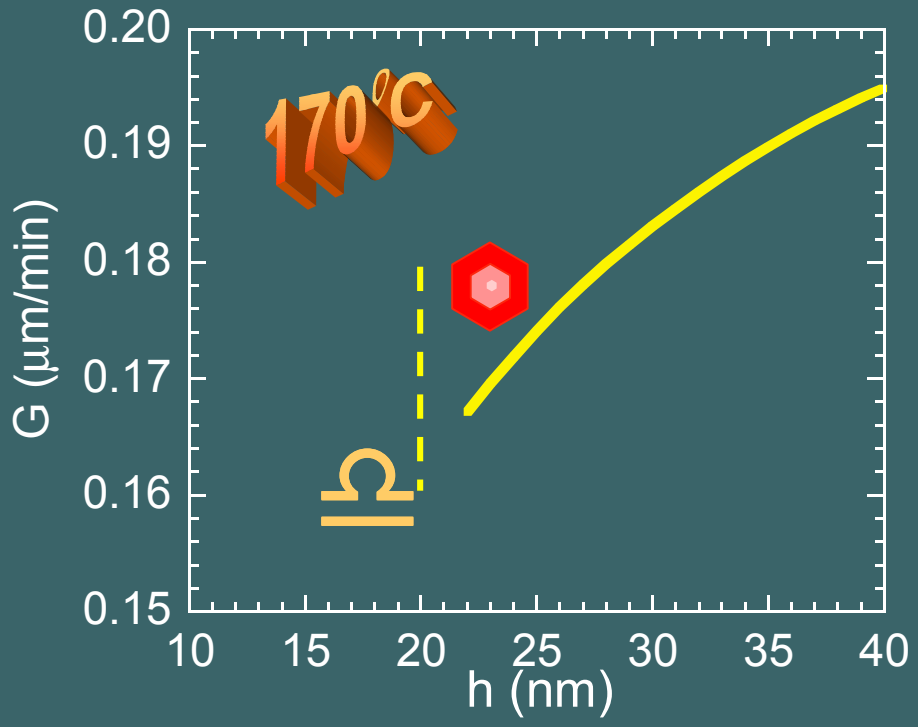
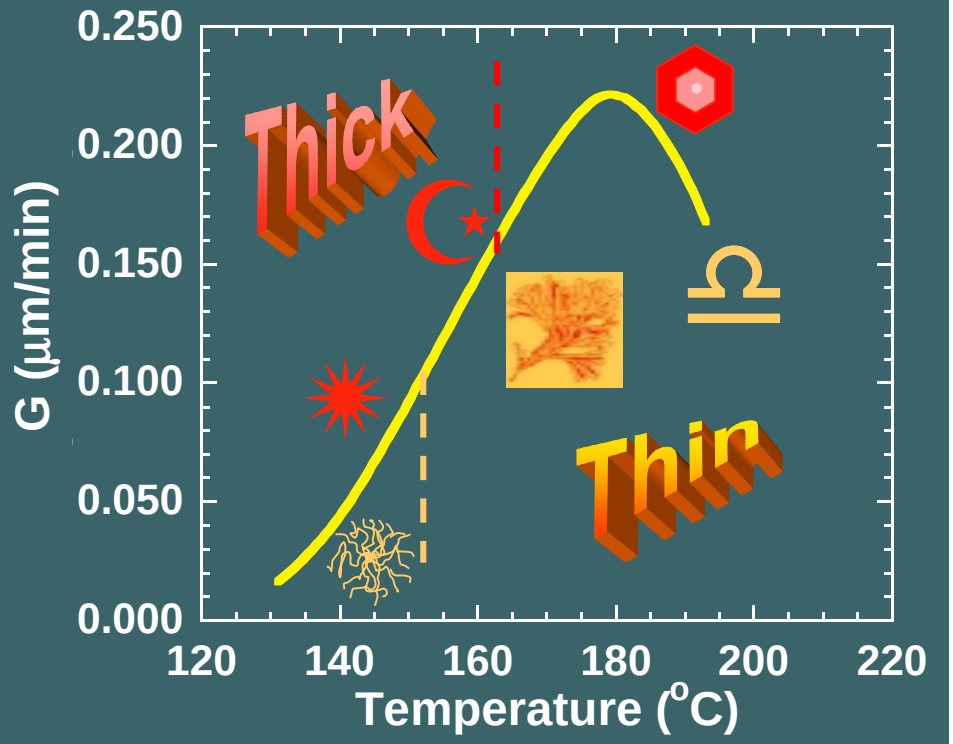
Confinement Effect

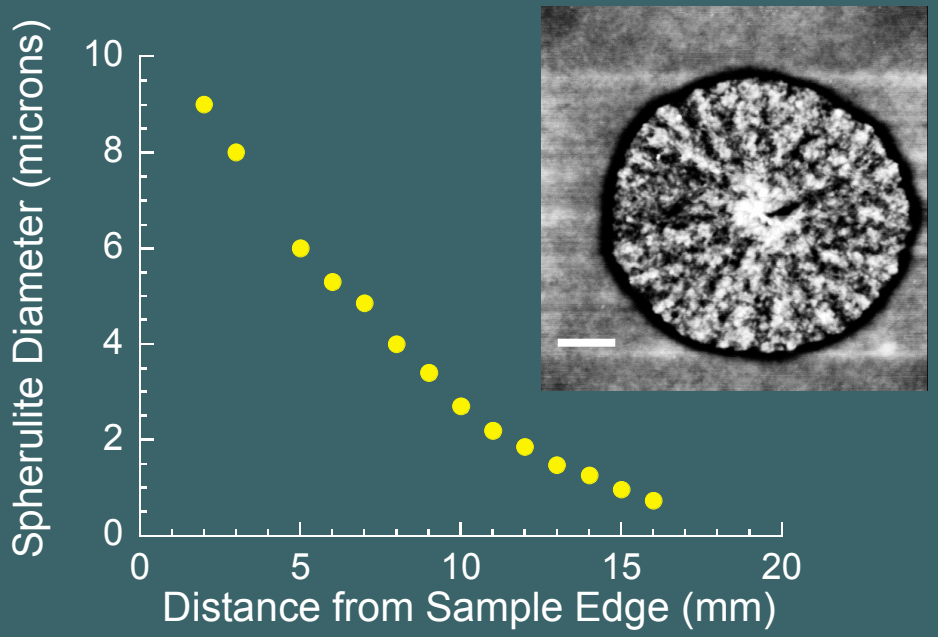


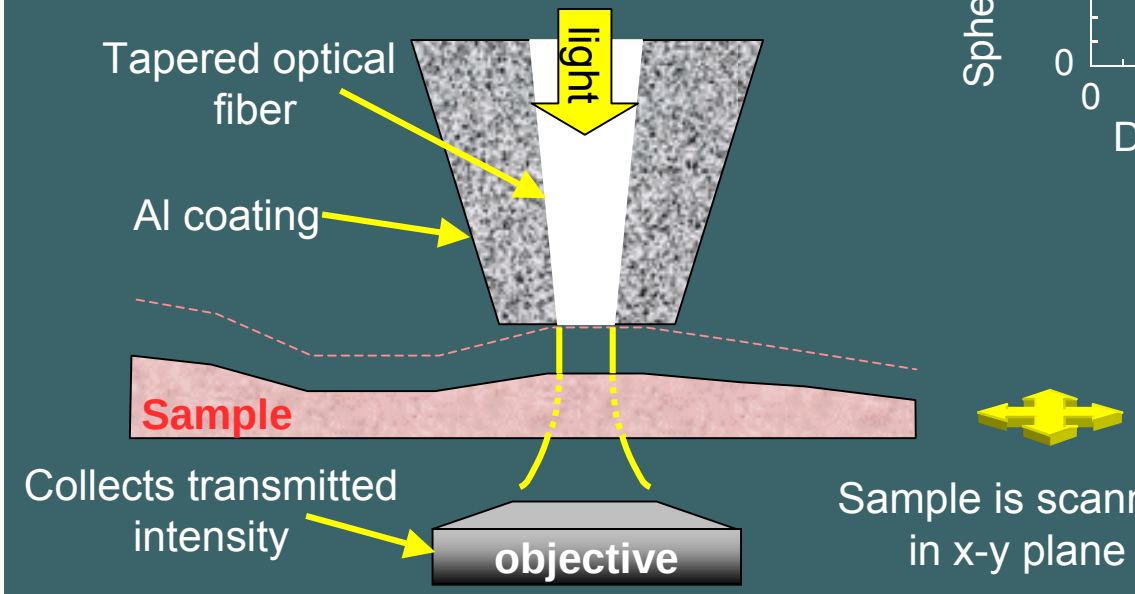
Viscoelastic Effect



Focusing on Target Areas: NSOM

Samples prepared on a shallow temperature gradient for short times can contain a narrow range of size and structures.





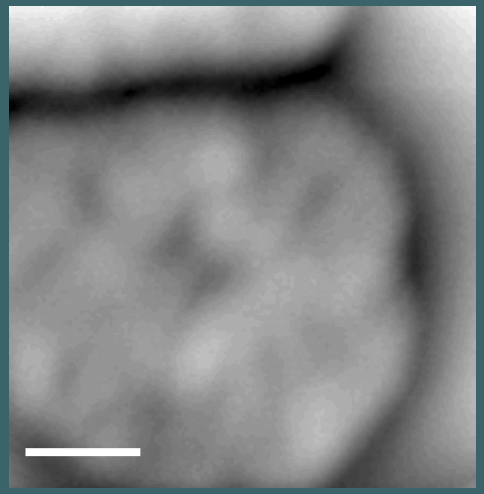
Sample is scanned in x-y plane

In collaboration with:
L. Goldner and M. Fasolka
Optical Technology Division
NIST

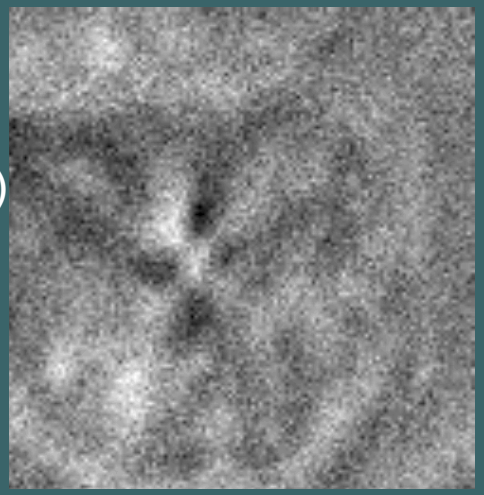
NSOM Polarimetry

L. Goldner and M. Fasolka,
Optical Technology, NIST

Topology (from force feedback)

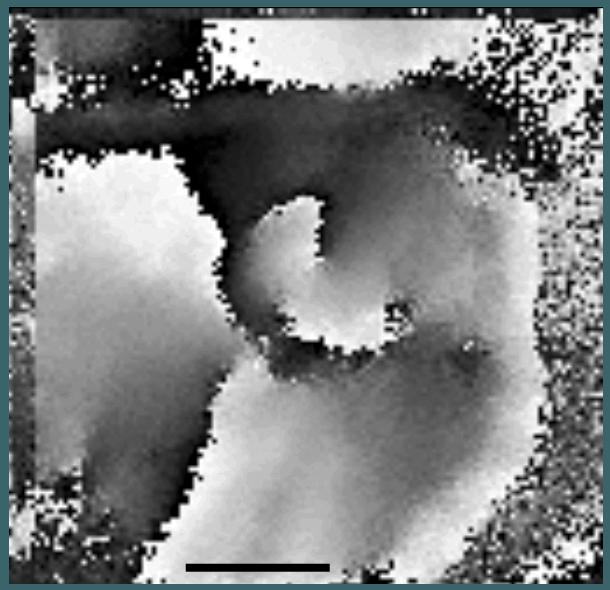


Dichroism (z-scale 0-4%)



Scale bars: 1 μm

Angle of Birefringence (z-scale 0-180°)



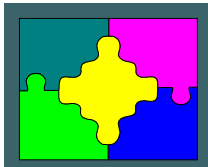
- NSOM polarimetry may provide insight into more complex optical activity for multiple crystal structures

Conclusions

- Crystal growth rates of isotactic polystyrene as a function of h and T on continuous gradient films agree with literature. G passes through a maximum near 180°C and decreases with h below 80 nm.
- Morphological transitions with T and h are similar to a recent publication. As h approaches R_g, spherulites are replaced by hexagonal dendrites.
- First evidence of competition between surface tension anisotropy and viscoelastic effects in crystallization.

Future Directions

- New measurement techniques
  - Mechanical and optical properties of semi-crystalline films
  - Kinetics in faster crystallizing films
  - Access to continuous parameter space on film
  - Structural probes during crystal formation
- Development of new informatics techniques (image analysis)
- Extension to polymers, blends and parameters of interest
  - iPP, PEG, PLA
  - Nucleating agents, surface energy or pattern gradients



Acknowledgments

Vincent Ferrreiro
Jim Warren

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Michael Fasolka

Archie P. Smith
Amit Sehgal
Alfred Crosby

$$
National Research Council